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The Renaissance of the Becker–Döring–Zeldovich Theory of Nucleation Kinetics

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The classical theory of nucleation kinetics was developed in works of Becker, Döring, and Zeldovich. The problem of huge discrepancy between experimental data about nucleation rate and theoretical results, based on the classical theory of nucleation kinetics, is discussed. Two drawbacks of classical theory are considered: application only isothermal nucleation kinetics and neglecting of microstructure of supersaturation field. It was shown that for the same temperature and supersaturation nonisothermal nucleation kinetics decreases the value of nucleation rate on 1–2 orders. For high nucleation rates the correct calculation of the microstructure of the supersaturation field can substantially, on several orders of nucleation rate, decreases this discrepancy.

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1. Introduction

Theory of the kinetics of the first order transitions has substantial scientific significance for deep understanding of many problems in physics and chemistry. Engineers widely used its results in development of numerous industrial reactors and processes.

One of the most interesting problem in this field is the formation of mesoscopic clusters in supersaturated medium. In particular, following to brilliant works of the first half of the twenty century made by Becker, by Döring, and, independently, by Zeldovich the formation of new phase clusters in supersaturated medium is considered as the Brownian motion over a thermodynamic barrier in cluster size space [1]. In spite of the beauty of this theory and its genuine insight, the discrepancy between experimental results and theoretical calculations is astonishing. For nucleation in supersaturated vapor the discrepancy can reach 12–20 orders of magnitude of nucleation rate [2]. It is worthy to note that experimental measurements of nucleation rate are usually smaller than theoretical results.

2. Nonisothermal nucleation

The classical theory of nucleation kinetics of vapors has one obvious drawback. It considers the kinetics of phase transition as isothermal process. But release of the latent heat of phase transition during condensation should lead to temperature difference between growing clusters and vapor - gas mixture. Only high enough energy transfer rate between molecules of carrier gas and growing clusters can eliminate this nonisothermal effect.

The use of methods of nonequilibrium statistical thermodynamics permitted the development of system of equations of nonisothermal nucleation kinetics [3]. For kinetic coefficients the expressions of Green–Kubo type have been obtained and they have been calculated at the free molecular regime. The simulation based on the derived equations of nonisothermal nucleation kinetics has shown that nonisothermal effects are responsible only for 1–2 orders of the famous discrepancy between the theoretical calculations and experimental data [4].

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3. Comparison with experimental data

During last two decades the results of careful steady-state measurements of nucleation rate of vapors have been published [2]. These results have been obtained by means of thermodiffusion cloud chambers and by different laminar flow diffusion chambers, which operate at the steady-state regimes. The discrepancy between experimental data and theoretical results was decisively shown by many groups of experimentalists. It is worthy to note that the count of newly formed droplets is based on optical measurements of scattering light. Thus radius of every counted droplet has to be about one micrometer or larger.

It is important to emphasize that all numerous attempts of the development of more sophisticated theories of nucleation kinetics have not decreased this discussed discrepancy.

The breakthrough has been made due to the idea of the microstructure of supersaturation field in experimental devices for nucleation studies [5]. For treatment of experimental data the supersaturation is calculated on the basis of heat and mass transfer equations.

Microstructure of supersaturation field results due to the feedback between growing cluster and the state of metastable medium near it. The important condition of formation microstructure is that the growth regime of a droplet is diffusion one. Near the droplet there is a relatively large volume where supersaturation value is significantly lower that the values calculated by means of standard mathematical model of heat and mass transfer. Let us consider the nucleation in vapors. In particular, it can be shown that in the laminar flow diffusion chamber if some droplet has grown up to a radius $10 \cdot \lambda$, where λ is the mean free pass of vapor molecules, then in the cylindrical volume $10^4\lambda^2\nu$ there is only the single new micron size droplet, ν is the mean velocity of gas. According standard calculation of nucleation kinetics it should be several thousands droplets [5]. It should be noted that the effect of the microstructure of supersaturation field is very profound for high pressure nucleation experiments.

4. Conclusions

Huge discrepancy between experimental results and calculations, based on classical theory of nucleation kinetics, is substantially decreased by taking into account two considered above effects: nonisothermality of kinetics and the microstructure of supersaturation field. Thus we can speak about some kind of the Renaissance of classical theory of nucleation kinetics. It is worthy to note that nonisothermality of kinetics is important only for nucleation in vapors.

No doubts that there are some fluctuations of thermodynamic properties of mesoscopic objects such as clusters of 100 molecules. These fluctuations should manifest themselve in stochastic fluctuations of nucleation rate. I guess that this effect is about one order of magnitude of steady state nucleation rate and should be taken into account in future development of nucleation kinetics.

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